Final Report

NASA, NAG5-6179, "Continuous Remote Measurements of Atmospheric O₂ Concentrations in Relation to Interannual Variations in Biological Production and Carbon Cycling in the Oceans"

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ABSTRACT

We successfully initiated a program to obtain continuous time series of atmospheric O_2 concentrations at a semi-remote coastal site, in Trinidad, California. The installation, which was completed in Sept, 1999, consists of a commercially-available O_2 and O_2 analyzers interfaced to a custom gas handling system and housed in a dedicated building at the Trinidad site. Ultimately, the data from this site are expected to provide constraints, complementing satellite data, on variations in ocean productivity and carbon exchange on annual and interannual time scales, in the context of human-induced changes in global climate and other perturbations. The existing time series, of limited duration, have been used in support of studies of the O_2/CO_2 exchange from a wild fire (which fortuitously occurred nearby in Oct., 1999) and to quantify air-sea N_2O and O_2 exchanges related to coastal upwelling events. More generally, the project demonstrates the feasibility of obtaining semi-continuous O_2 time series at moderate cost from strategic locations globally.

KEY WORDS

atmospheric oxygen, carbon cycle, ocean productivity, coastal upwelling

PROJECT OVERVIEW

The purpose of this proposal was to assess the feasibility of producing continuous records of variations in atmospheric O_2 concentration at baseline sites in order to resolve signals related to annual and interannual variations in marine biological production and carbon cycling in the oceans. Continuous O_2 time series are needed, as a complement ongoing flask programs, to improve the ability to detect small shifts in the amplitude and phasing of the seasonal O_2 cycles associated, for example, with plankton blooms or winter-time convective mixing in the high-latitude oceans. Continuous O_2 time series would complement satellite-derived ocean color datasets by providing additional constraints on large-scale organic carbon fluxes and by providing an independent index of interannual variations in marine biogeochemistry. Such data would also provide tests of the sensitivity of marine biology to changes in climate, stratospheric ozone, nutrient availability, or other perburbations, and would aid in validating models of ocean primary productivity driven by satellite-derived ocean color datasets.

The scope of the project involved developing field instrumentation, including a paramagnetic O₂ analyzer and a non-dispersive infrared (NDIR) CO₂ analyzer, and deploying this instrumentation at Trinidad Head, California, as an initial field test site. The project was essentially a proof-of-concept exercise to assess the practicality of making time-series measurements with continuous O₂ sensors from semi-remote sites. Collecting a year or so of data from a single station, as proposed, was clearly only a first step in this project, as the main payoff would come from collecting 5 to 10 years of data, perhaps from several such sites. The Trinidad site is one of several sites of the Advanced Global Atmospheric Gases Experiment (AGAGE) network, a complementary NASA effort to obtain global atmospheric time series of CFCs, HFCs, methane, and nitrous oxide, as well as other trace gases.

As discussed in more detail below, the project as a whole was highly successful. By the end date of this project (8/14/2001), we had obtained 22 months of semi-continuous data. We encountered relatively few problems in maintaining the instrumentation with only modest oversight (\sim 1 visit weekly by a technician). Although 22 months of data is insufficient to address questions of interannual variability, the data already showed some novel features of considerable interest. Among these was clear evidence of signals in the O_2 concentration related to episodes of enhanced coastal upwelling and water ventilation, which we have found useful for quantifying coastal exchanges of other gases, principally nitrous oxide, as described further below.

DESCRIPTION OF ANALYZER AND GAS HANDLING SYSTEM

The analyzer and gas handling system are show in Figure 1. Instrument diagnostics and data collection were both enhanced by changing the design to locate the LICOR CO₂ analyzer upstream of the paramagnetic analyzer. The LICOR and gas handling system are mounted on the instrument rack as shown in Figure 2, with the paramagnetic analyzer located to the left. Instrument automation and control programming is written with Labview software (obtained from National Instruments), with the data collection and transfer to Scripps implemented with both Labview and PC-Anywhere software.

DESCRIPTION OF INSTALLATION AT TRINIDAD

After considering the costs and benefits of building a laboratory vs. obtaining a pre-fabricated container and shipping it to the site, we opted for building an 8ft. by 16ft. laboratory at Trinidad Head. Prior to construction, approval was obtained from the U.S. Coast Guard, including a building permit waiver obtained from the California Coastal Commission, and an environmental impact assessment. The building was designed in house and built with the assistance of a local contractor from Trinidad. The paramagnetic analyzer is sensitive to vibrations, and thus requires a very stable platform. A concrete pedestal was included in the foundation to accommodate the analyzer and provide a vibration free support in the middle of the laboratory (Figure 3). The location of the building is shown next to the antenna that supports the air intake line in Figure 3. The operation of the facility required that new electrical and phone service be installed in the completed building (Figure 4).

SUMMARY OF INSTRUMENT CALIBRATIONS AND PERFORMANCE

Since the installation of the paramagnetic analyzer in October 1999, the instrumentation has performed nearly continuously, as indicated in Figure 5. Two brief interruptions in 10/99 and 11/99 were due to air pump failure. A second system problem due to a leaky switching valve was detected and repaired on 3/6/01. At this time a monthly High Span gas was added to the calibration scheme. Calibration of the non-linearity of the LICOR CO₂ analyzer with 6 primary gas cylinders prepared at SIO (traveling primaries) was performed on 4/28/00, 7/31/00, and 9/28/01.

PROJECT HISTORY AND MILESTONES

7/1/97 Project start date

1/31/98 Initial Site Visit

8/98 Tim Lueker hired to serve as project manager.

1/98-6/99 Construction and initial testing of paramagnetic unit and handling system at Scripps.

11/6/98 Agreements finalized with U.S. Coast Guard and the California Coastal Commission to on permission to install the remote laboratory.

12/98 Initial construction phases of laboratory building on Trinidad Head site.

7/99-8/99 Interfacing paramagnetic unit with air supplied from the end of the Pier located at the Scripps Institution of Oceanography for testing and diagnosis of real-time continuous atmospheric sampling, prior to deployment at Trinidad Head.

8/99 Presentation of initial paramagnetic analyzer results at the Gordon Conference on Chemical Oceanography during the keynote address.

9/99-10/99 Completion of building and installation of instrumentation at Trinidad Head.

11/9/99 Host scientists at 20th meeting of AGAGE at Trinidad Head. Present initial results from analyzer O₂ and CO₂ data.

10/17/00 Attend 22^{nd} meeting of AGAGE scientists at Kona, Hawaii. Presented the results of the first year of data from Trinidad Head, including evidence of upwelling induced variability in O_2 and N_2O .

10/00-8/01 Development of Matlab routines for data synthesis and analysis

2/2001 Presentation at ASLO meeting in Albuquerque NM. (see below)

PUBLICATIONS RESULTING FROM PROJECT:

(1) 2001, The Oxygen to Carbon Dioxide Ratios observed in Emissions from a Wildfire in Northern California. <u>Geophys. Res. Lett.</u> Vol. 28, no. 12, 2413-2417.

Abstract. At Trinidad, California we observed elevated CO_2 concentrations and concomitant lowered O_2 levels coincident with forest fires 70 km distant (from 10/8/99 to 10/21/99). The precision of our O_2 data, \pm 1 μ mol O_2 /mol dry air, revealed the reduction of atmospheric oxygen resulting from the combustion of biomass, and the stoichiometric ratios ($-O_2/CO_2$) of the wildfire emissions. Estimates of daily $-O_2/CO_2$ ratios were obtained by regression of CO_2 against corresponding O_2 data (O_2/CO_2). Daily O_2/CO_2 ratios changed from 1.15 to 1.41 on a particularly smoky day that coincided with elevated levels of CO_2/CO_2 ratios and increased CO_2/CO_2 ratios. The change to a higher ratio during smoky conditions illustrates the association between changing emissions and O_2/CO_2 ratios, possibly due to changing wildfire dynamics.

- (2) 2001, Air-sea fluxes of oxygen and reactive trace gases revealed in continuous records of atmospheric oxygen and carbon dioxide at Trinidad, California., ASLO published abstracts http://aslo.org/albuquerque2001/650.html
- (3) Continuous records of atmospheric Oxygen, Carbon Dioxide and Nitrous Oxide in Northern California reveal air-sea fluxes enhanced by coastal upwelling (manuscript in preparation).

Abstract: Background levels of nitrous oxide, methane, chlorofluorocarbons and other trace gases have been monitored continuously at Trinidad Head, California, since 1995. A separate facility, added in October 1999 provides continuous records of atmospheric oxygen (as O2/N2) and carbon dioxide. Along with seasonal and diurnal cycles in O₂/N₂ we have observed episodic negative anomalies, lasting several days, coincident with sustained NNW winds and reduced ocean surface temperatures. Elevated levels of atmospheric N2O closely followed the episodic reductions in O₂/N₂. Hydrographic profiles of dissolved O₂ and N₂O from the coastal NE Pacific suggest that ventilation of upwelled water depleted in O2 and enriched in N2O resulted in the anomalous atmospheric concentrations. We estimated sea-air fluxes of O_2 and $N_2O > -1.5$ mol m⁻² dy⁻¹ and 5x10⁻⁵ mol m⁻² dy⁻¹ respectively (positive flux to atmosphere) by evaluating atmospheric transport from meteorological observations and scatterometer derived wind stress fields. We verified the potential for ocean fluxes of this magnitude from the few available coastal north pacific hydrographic profiles of temperature, dissolved O2, and N2O by estimating air-sea concentration differences and gas exchange coefficients (formulated as a function of ocean temperature and wind speed during upwelling events). Our estimates of air-sea fluxes of both O2 and N2O derived from atmospheric measurements agree with fluxes predicted from regional hydrographic data when observed temperature / dissolved O2 / dissolved N2O relationships are extrapolated to surface ocean temperatures observed during the upwelling events.

Figure 1. Continuous O2 and CO2 analyzer at Trinidad Head

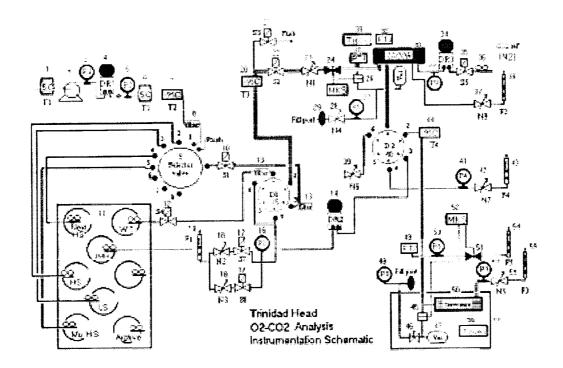


Figure 2. Paramagnetic analyzer instrumentation developed for Trinidad Head.

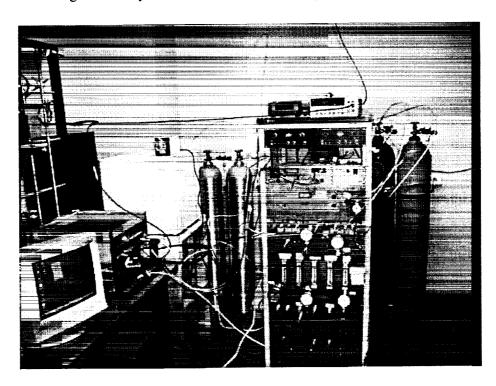
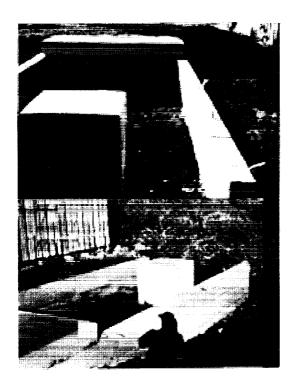


Figure 3. Trinidad Head Building Site



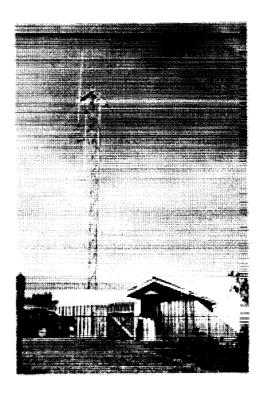


Figure 4. Electrical phone and instrument installation at finished building site at Trinidad Head.



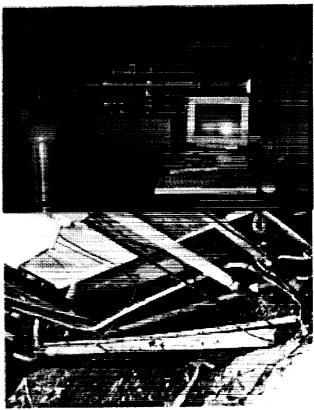
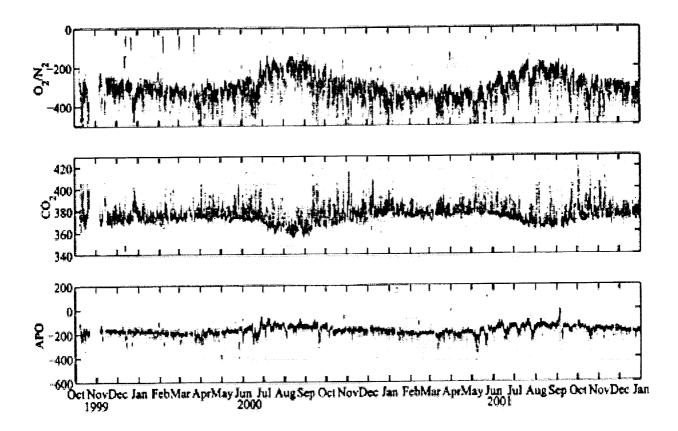


Figure 5. Record of paramagnetic Oxygen and Licor CO2 analyzer performance at Trinidad Head The third panel shows the tracer atmospheric potential oxygen (APO), where APO \sim O₂ + 1.1*CO₂+ const., which effectively measures the oceanic contribution to the atmospheric oxygen changes. Periods of several days can be seen during which APO makes excursions towards lower values, reflecting oceanic O₂ uptake associated with episodic coastal upwelling. Further details can be found on the web at: http://bluemoon.ucsd.edu/tim/tim_web/Research/research.html



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